Text to the poster report

A MATHEMATICAL MODEL OF MODIFICATION OF POLYETHYLENE SURFACE BY LOW INTENSITY AND LOW ENERGY PRESSURE IN RF DISCHARGE AT LOW PRESSURE[1]

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Abstract

A molecular-dynamic model of UHMWPE surface modification by a low-intensity flow of low-energy Ar ions generated by a low-pressure RF discharge is considered. It was found that ion bombardment initiates the rupture of intramolecular bonds and the formation of radicals on the UHMWPE surface, it takes on hydrophilic properties as a result.

Introduction

The processing of materials in a radio-frequency (RF) discharge in a dynamic vacuum is an effective way of surface nanostructures modifying [1]. First, a few words about RF discharge in a dynamic vacuum is and a difference one from other types of radio-frequency discharges.

1. RF discharge in dynamic vacuum

When we say "dynamic vacuum" we mean a dynamic mode of vacuum, when gas is supplied to the vacuum system and pumped out continuously, i.e. there is gas movement in the device. Our operating pressure range is from13.3 to 133 Pa, plasma gas flow rate is in range from 0.02 to 2.5 g/s. The RF discharge is generated in a discharge tube 2.4 cm in diameter using a solenoid in inductive coupled RF (ICRF) discharge (Fig. 1*a*) or external cylindrical electrodes in capacitively coupled RF (CCRF) discharge (Fig. 1б). Due to gas flowing, the plasma is flowed into a vacuum chamber with diameters of 0.3-0.5 m, where the plasms flux forms a jet (Fig. 1*в*). The plasma jet is reached up to 0.5 m in some discharge modes. The last is a main visually difference between RF discharges under dynamic vacuum and both non-flow RF discharges and ICRF discharge of atmospheric pressure, in which the length of the plasma jet is about 3 cm.

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[1] On the poster, the title of the report is streamlined for technical reasons.

2. Characteristics of HF Discharges in Dynamic Vacuum

Measurements of the characteristics of RF discharges under dynamic vacuum also showed significant differences from other forms of RF discharges. Thus, in the vacuum chamber, quite high values of the magnetic field strength, current density (Fig. 2), and electron density (Fig. 3a) are found, which are several orders of magnitude higher than in case if the jet were a stream of decaying plasma.

Three factors such as low pressure, gas flow, and high values of field strength and electron density, create special conditions for specimen processing: high thermal nonequilibrium (electron temperature is in range (1-4) 10^4 K whereas the temperature of atoms and ions is in range (3-7) 10^2 K), a positive sheath (PS) of 2-5 mm in a thickness is raised near the surface of the sample. In fig. 3b, the PS region is marked with white circles. The density of ions in the PS is significantly higher than the density of electrons. The PS near the sample surface in a plasma jet arises for the same reason as the near-electrode PS's in an CCRF discharge, namely, as a result of electron oscillations in the RF field with respect to low-mobile ions [2]. Plasma ions are accelerated in the PS electric field to energies of ~ 10-100 eV at an ion current density of 0.05 to 8 A / m^2 (Fig. 4).

Thus, an RF discharge in a dynamic vacuum is a source of a low-intensity flux of low-energy ions.

3. Surface modification of ultra-high molecular weight polyethylene

Due to the low gas temperature, low ion current density on the sample surface, and relatively high ion energy in the plasma jet, it is possible to efficiently process materials that lose their mechanical and physical properties upon heating, for example, polymers. One of the widely used materials is ultra-high molecular weight polyethylene (UHMWPE), the fibers of which exceed the tensile strength of steel. However, its applications are limited by its hydrophobicity.

UHMWPE acquires hydrophilic properties after treatment by an RF discharge under dynamic vacuum in an argon atmosphere (Fig. 5), which significantly improves the adhesive strength of composite materials based on UHMWPE [4]. As a result of treatment, free radicals are formed on the surface, which react with atmospheric oxygen and form hydrophilic functional groups. At the same time, a number of questions about the mechanism of modification remain unclear. the mechanism of interaction of plasma with the surface of polymeric materials is possible to study in detail including during the process of plasma exposure by the molecular dynamics [4].

The aim of this work is to study the mechanism of modification of UHMWPE in RF discharge by classical molecular mechanics.

4. Low-energy ion bombardment model

Polyethylene $[-CH2-]_n$ is a product of ethylene polymerization. Polyethylene belongs to crystal-amorphous polymers. The proportion of crystalline regions in UHMWPE reaches 95-97%. The packing of macromolecules in a crystallite is orthorhombic. Therefore, a crystalline region was considered in the model in the case when the zigzag plane is oriented parallel to the surface. Modeling was carried out for a polymer unit cell with a size of 9x7.6x75 nm^3.

The model is described by a system of equations of motion of interacting particles:

$$\frac{d\mathbf{v}_k}{dt} = \frac{1}{m_k}\sum_{k\neq l} \mathbf{F}_{kl}\,,\quad k = 1, \dots, N+1, \qquad \frac{d\mathbf{r}_k}{dt} = \mathbf{v}_k, \qquad (1)$$

$$\mathbf{v}_k(0) = \begin{cases} 0, & k = 1, \dots, N, \\ \sqrt{2W_i/m_i}\,, & k = N+1, \end{cases} \qquad \mathbf{r}_k(0) = \mathbf{r}_{k0}, \qquad k = 1, \dots, N+1. \qquad (2)$$

Here $\mathbf{v}_k$ is the velocity vector of the *k*-th particle, $\mathbf{r}_k$ is its radius vector, $\mathbf{r}_{k0}$ are the coordinates of the initial position of the particles, $\mathbf{F}_{kl}$ is the force acting on the kth particle from the *l*-th particle, m_k is the mass of the k-th particle $(k = 1, \dots, N)$, $m_{N+1} = m_i$ is the mass of the bombarding ion, W_i is ion kinetic energy, *t* is the time, *N* is the number of atoms in the model cell of the material, the particle with the index *N*+1 corresponds to the incident ion. The forces of interaction of the k-th и l-th atom $\mathbf{F}_{kl}$ are set using paired or many-particle potentials, $\mathbf{F}_{kl} = -\mathrm{grad}\, U_{kl}$, where U_{kl} is calculated as the sum of the potentials of valence and non-valence interactions.

We considered the all atom model as the Lennard-Jones (LJ) potential U_{kl} with long-range Coulomb forces, AIREBO-M [5], and ReaxFF [6]. The interaction of an argon atom with polyethylene macromolecules was modeled using the Lennard-Jones potential.

The Verlet algorithm was used for solving the system (1)-(2). The model was implemented using the LAMMPS package [7, 8]. The numerical integration of the system of equations (1)-(2) was carried out with a time step δt = 0.1 fs. The calculation results were visualized in VMD and OVITO packages.

The most acceptable situation from the point of view of compliance with the existing concepts of the interaction between low-energy ions and materials is given by the AIREBO-M potential. It was found that at an ion energy of 10 eV, there are no significant changes in the PE structure. At energies of 50 eV and 100 eV, a track and short alkene radicals are formed around a moving Ar atom, and several hydrogen atoms are also ejected from the surface. The penetration depth of the Ar ion into the unit cell was determined as the distance at which the ion lost energy until decelerated. The penetration depth of an argon atom at an energy of 50 eV is 1.8 nm, and at an energy of 100 eV, 2.8 nm.

The simulation results showed that the sputtering coefficient is from 1 to 5 particles, depending on the energy of the incident particle. Sputtered particles are short-chain radicals $[-CH2-]_n$, n = 2 ÷ 6.

Thus, a result of argon ion bombardment is the destruction of the UHMWPE molecules. Particles of truncate molecular compounds ((poly-) alkenes, (poly-) alkyls) can appear. Short radicals leave the cell surface forever, more longer radicals remain inside the cell. In this case, a noticeable track is formed along the trajectory of the ion, which is disrupted chains of PE molecules and filled with shorter radical residues, in accordance with the theory of a local thermal peak.

5. Conclusion.

RF discharge under dynamic vacuum mode forms the plasma jet up to 0.5 m in length, so sufficiently high values of the magnetic field strength, current density, and electron density are observed. Due to the high thermal nonequilibrium $T_e/T \sim 10 - 100$ and the formation of a layer of positive sheath, the sample surface is subjected to ion bombardment with the energy from 10 to 100 eV at the ion current density $j_i = 0.02 - 8$ A/m^2.

Low-energy low-intensity ion bombardment leads to the rupture of intra- and intermolecular bonds, as a result long-lived radicals of the residues of molecular chains are formed on the surface of UHMWPE.

Active low-mobility radicals react with atmospheric oxygen when the samples are removed from the vacuum chamber after plasma treatment. Functional carbonyl groups (–C = O) appear on the surface of UHMWPE fibers, as a result of which the surface of UHMWPE acquires hydrophilic properties.

Thus, modeling shows that, due to the rupture of intermolecular and interatomic bonds and low-energy ion implantation, uncompensated carbon bonds with a long lifetime, capable of forming functional groups after plasma treatment, appear in the surface nanolayer. In the case of intermolecular penetration of implanted ions, stressed states arise in the surface layer, due to this, the surface energy increases. The combined effect of these factors contributes to the activation of the surface and an increase in the adhesion of UHMWPE fibers to the matrices.

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